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Characterization of Membranes for Fuel Cell Applications: Challenges in Translating Ex-situ Properties into In-situ Performance

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1 Introduction

For automotive or stationary applications of PEM fuel cells several advantages result by operating under elevated temperature (> 100 °C) and low relative humidity (< 35 %) conditions, such as more efficient heat and water management, higher reaction rates and improved tolerance against catalyst poisoning. However, under these conditions dehydration and degradation of state-of-the-art PFSA membranes result in an enhanced loss of conductivity and cell performance. For this reason novel membrane concepts (e.g. composite membranes with inorganic additives) as well as more specific and reliable test schemes are needed to reflect the fuel cell operation under hot and dry conditions.

This paper addresses different material concepts with respect to low rH / high temperature conditions. Furthermore specific considerations from an MEA manufacturer's perspective in applying characterisation techniques, designing efficient test protocols to identify membrane materials with improved properties and translating ex-situ data into in-situ performance will be discussed.

An integrated test scheme for composite membranes can be subdivided in ex-situ and in-situ experiments.

(a) Determination of intrinsic membrane properties in ex-situ experiments such as ionic conductivity by impedance spectroscopy (EIS), mechanical properties by dynamic mechanical thermal analysis (DMTA) under humidity cycling protocols, accelerated aging by Fenton's Test, electrochemical stability and mobility of inorganic additives by cyclic voltammetry.

The data from those tests supports the screening of membrane materials and suitable candidates are identified for more complex in-situ experiments.

(b) In-situ experiments with membrane-electrode-assemblies in a single test cell are standard protocols to test performance as against reference MEAs (e.g. based on a design with a catalyst coated GDL), protocols reflecting hot and dry operating conditions to gather performance data relative to standard materials and specific protocols aiming at accelerated aging. To investigate membrane specific failure modes in-situ experiments have to be accompanied by several diagnostic tools, such as cyclic or linear sweep voltammetry to measure hydrogen crossover, electrical shorts and stability of inorganic additives. Hydrogen pump can be used to monitor DC membrane resistance.

Lifetime and durability are critical issues in fuel cell systems. In useful lifetimes the membrane-electrode-assembly (MEA) is the most limiting component of such systems. In order to develop materials with enhanced lifetime and better durability a sound understanding of failure modes such as membrane thinning and catalyst degradation during

fuel cell operation is needed. Hence the application of accelerated aging tests and life time models are important tools in the development of membrane-electrode-assemblies.

2 Membrane Concepts

The state-of-the-art proton exchange membrane (PEM) materials for fuel cells are based on perfluorinated sulfonic acids (PFSA). The limitation to operate those PFSA-based PEM-fuel cells under low relative humidity or even without external humidification is mainly based on the fact that proton conductivity of the membrane will decrease significantly. That restriction is the main driver for developing novel membrane materials. Besides conductivity those materials have to fulfil various other properties:

- high proton conductivity
- low electrical conductivity
- low H_2 and O_2 crossover, but high enough oxygen solubility to allow good cathode ORR reaction
- good water permeability / diffusivity
- oxidative and hydrolytic stability
- mechanical integrity and dimensional stability

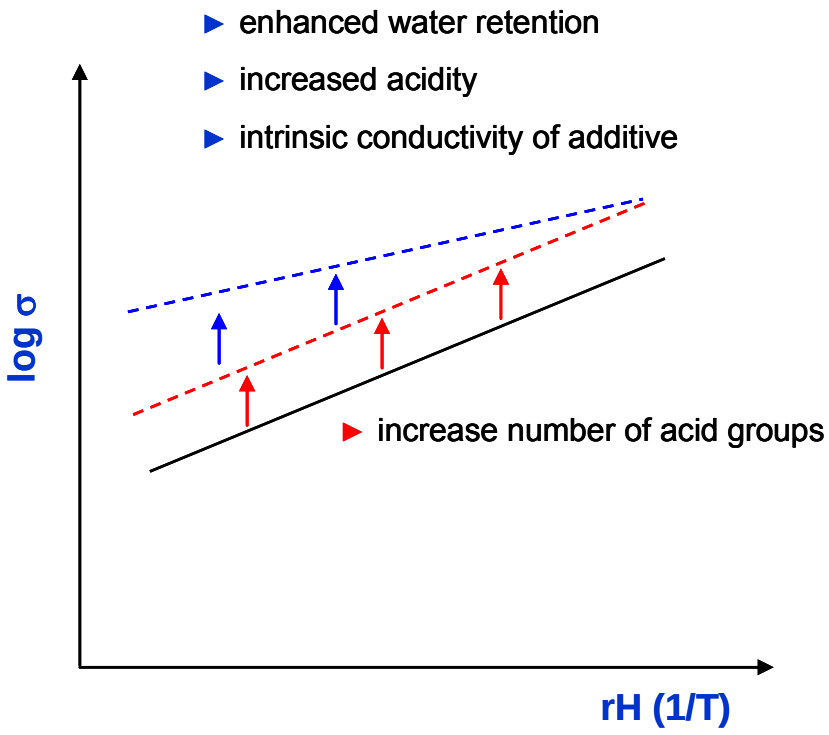

Figure 1: Influence of different material approaches on proton conductivity.

The scheme in Figure 1 shows how different material concepts could address an increase in proton conductivity as a function of relative humidity (or inverse temperature at constant dew point). Increasing the number of acid groups - reducing the equivalent weight at a given

molecular weight - would shift the proton conductivity to higher values however with the same sensitivity towards relative humidity expressed by the slope of the plot. By enhancing water retention and / or increasing the acid strength also the slope of the σ-rH-characteristic could be addressed.

Reducing the equivalent weight at a given molecular weight however will be accompanied with a lower degree of crystallinity and the membrane will compromise in its mechanical properties and integrity. The solubility increases with lower equivalent weight where the crystallity goes to zero and many mechanical properties parallel this effect. The experimental data in Figure 2 shows the proton conductivity for two different humidity conditions (T = 80 °C, DP = 80 °C and T = 120 °C, DP = 80 °C) as a function of equivalent weight.

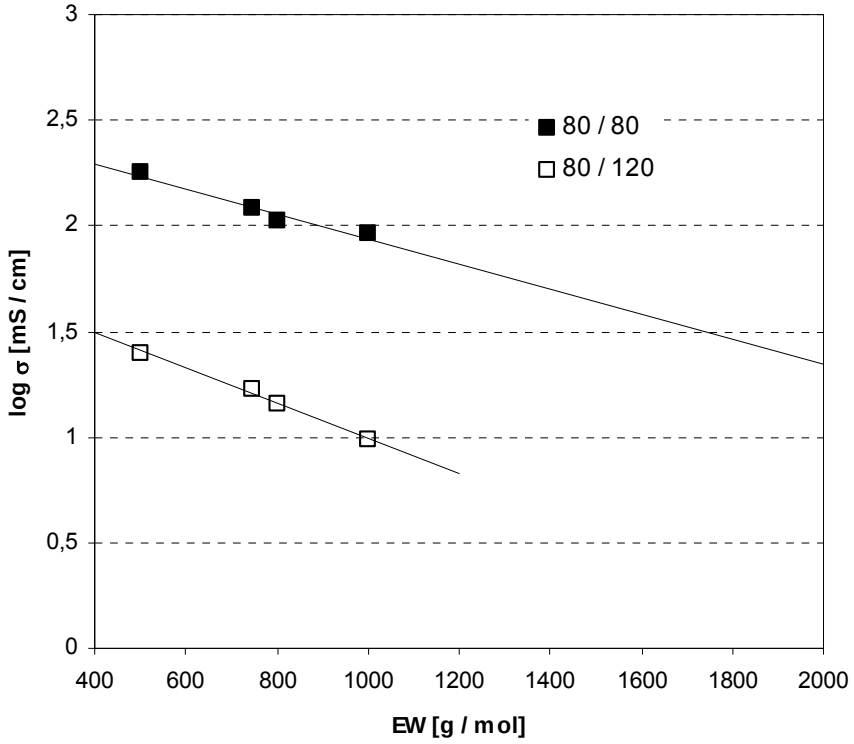

Figure 2: Proton conductivity for PFSA-based membranes as a function of equivalent weight (EW).

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